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COMPARATIVE STUDY BETWEEN KINETIC AND THERMODYNAMIC CALCULATION OF COMPOSITION IN SF₆ PLASMAS

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ABSTRACT

For an SF₆ plasma at atmospheric pressure the compositions calculated in chemical equilibrium, in the multi-temperature model and using kinetics (33 reactions involving 18 species) are compared. The ratio of the electron temperature T_e to that of heavy species T_h was calculated as a function of electron density and an intermediate temperature T^* between T_e and T_h was introduced to cope with the relationship $k_f(T^*) / k_r(T^*) = K_x(T^*)$ where k_f and k_r are the reaction rate coefficients (forward and reverse) and K_x the equilibrium constant. The main difference between equilibrium and kinetic calculations lies in the densities of S⁺, S₂⁺, SF⁺, F⁻ and S⁻ species between 2000 and 6000 K. The multi-temperature method gives results very different from those of the kinetic calculations even when neglecting the charge loss reactions. This is in contrast to what happens with H₂ or N₂.

Key words: SF₆ plasma composition, multi-temperature

1- Introduction

A plasma, whatever might be its composition, must be maintained by conservation of its constituents as well as an input of energy (a current due to the existence of an electric field in a thermal plasma). The balance of energy gain (heating) and loss (cooling) of the heavy particles and electrons in the plasma is time and location dependent and is very seldom in perfect equilibrium. In order to determine the plasma flow and the resulting momentum, heat and mass transfers to a material to be treated the degree of non-equilibrium must be determined. It allows to calculate the plasma composition, its transport properties and then the flow properties.

Many works have been devoted to the non-equilibrium problems using either multi-temperature mass action law, equivalent to Gibbs free energy minimization [1-5] including multi-temperature partition function calculations [6-8], or kinetic calculations [9-10] or even collisional-radiative models [11].

For all methods the question is : what is the relationship between the electron temperature T_e and that of heavy species T_h when the electron density varies ? An approach has been proposed by André et al [12] where the ratio $\theta_e = T_e/T_h$ depends on $\ln(n_e/n_e^{\max})$

$$\theta_e = 1 + A \cdot \ln(n_e/n_e^{\max}) \quad (1)$$

n_e^{\max} being the electron density over which equilibrium can be assumed. The values chosen for n_e^{\max} and A are $n_e^{\max} = 10^{23} \text{ m}^{-3}$ and $A = -0.2$ in such a way that $\theta_e = 2$ at 5000 K and $\theta_e = 1.2$ at 9000 K in agreement with experimental values [13,14]. However, even when using the method of André et al [12] a problem is still pending when calculating the forward k_f and reverse k_r kinetic reaction rate coefficients. For instance, in the reaction $\text{SF}^+ + e \rightarrow \text{S} + \text{F}$, how to keep the relationship $k_f / k_r = K_x$, where K_x is the equilibrium constant, with a forward reaction linked to inelastic collisions with electrons and calculated at T_e while the reverse reaction involves collisions between heavy species with k_r calculated at T_h ? To solve that problem a temperature T^* between T_e and T_h has been introduced in such a way it tends towards T_h when n_e is low and towards T_e when the densities of neutral species are low [15] :

$$T^* = T_e - (T_e - T_h) \exp(-R) \quad (2)$$

To fulfil these requirements R has been defined as the ratio of the electron flux to that of neutral species

$$R = n_e v_e / \sum_i n_i v_i \quad (3)$$

v_e and v_i being calculated easily by assuming Maxwellian distributions.

A systematic comparison of the results obtained by using the kinetic calculations and the Gibbs free energy minimization has been performed recently [15] for hydrogen and nitrogen plasmas. This study has shown that the leading reactions were those with low activation energies. The purpose of this work is to determine for a much more complex mixture such as that resulting from the heating of SF_6 which are the key reactions controlling the kinetics and compare the results with those of equilibrium calculations and multi-temperature mass action laws calculated at T^* .

2- Reactions and kinetic data

2-1. General remarks

According to the chosen method, the nonequilibrium ratio θ_e as well as the temperature T^* , defined in eqns (1) to (3), depend strongly upon the result of the calculation through the species densities and the only mean to change them is to adjust for example the

constants A and n_e^{\max} (see eqn(1)). This method is not developed to determine precisely densities of the minor species for which the nonequilibrium effects may be drastic but to evaluate how it affects the major species on which the flow depends. As long as only the free flow calculation is considered no reactions at the wall have been taken into account.

2-2. Kinetic data

33 reactions implying 18 different species have been considered. Most of them are those proposed by Cliteur et al [5] and in table 1 are summarized only those which are not proposed by Cliteur or we have preferred. The reactions have been written as:

$$k_f = A(T_{g,e} \text{ or } T^*)^B \exp(-e\hat{C}/k(T_{g,e} \text{ or } T^*)) \quad (4)$$

the reverse reaction being determined by

$$k_r = k_f(T_{g,e} \text{ or } T^*) \cdot \Pi Z_{\text{reac}}(T_{g,e} \text{ or } T^*) \cdot \exp(e\hat{E}/k(T_{g,e} \text{ or } T^*)) / \Pi Z_{\text{prod}}(T_{g,e} \text{ or } T^*) \quad (5)$$

Z being the partition function either of the reactants or of the products, \hat{C} the activation energy, \hat{E} the reaction energy and e the electronic charge. Π represents the product of partition functions.

Number	Reaction	A	B	\hat{C} (eV)	\hat{E} (eV)
1	$F + e \rightarrow F^+ + 2e$	$5.0 \cdot 10^{-7}$	- 1.500	17.423	17.423
2	$F^+ + S_2 \rightarrow S + S^+ + F$	$3.0 \cdot 10^{-16}$	0	0	- 6.461
3	$F^+ + SF \rightarrow S^+ + 2F$	$3.0 \cdot 10^{-16}$	0	0	- 9.123

Table 1. Considered chemical reactions different from those of Cliteur [5] for the kinetic approach

The partition functions necessary for eqn(5) were calculated using the method proposed by Aubreton et al [7] for different temperatures.

3- Results and discussion

3-1. Equilibrium calculation

The evolution of the different species density with temperature at atmospheric pressure starting from 1 mole of SF_6 is represented in fig 1a from 4000 to 15000 K and in fig 1b from 1000 to 6000 K. Over 6000 K practically all the species are dissociated and the main ions are S^+ and F^+ with less than $5 \cdot 10^{-19} \text{ m}^{-3}$ F^- ions. Below 6000 K many molecules exist and the ionized species between 2700 and 3500 K are exclusively S_2^+ and F^- , S^+ and electrons starting

to show up, at least for $n_i > 10^{18} \text{ m}^{-3}$, respectively at 3500 K and 3900 K. These results are in good agreement with the published previous results [11].

SSFF and FSSF correspond to two isometric forms of S_2F_2 .

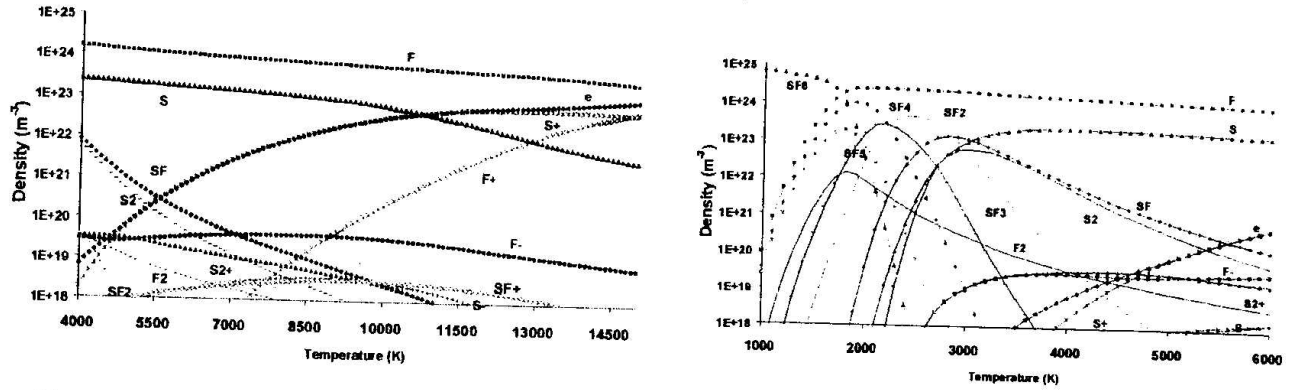


Fig 1: Equilibrium composition at atmospheric pressure of an SF_6 plasma starting from 1 mole of SF_6 a/ up to 15000 K with only diatomic molecules, atoms and ions represented, b/ up to 6000 K.

3.2. Multi-temperature calculation at T^*

They have been performed at T^* (see eqns(2) and (3)) with eqn(1) allowing to determine θ_e thanks to an iterative procedure. Fig 2 represents the variation of T_e and T^* with T_h . Over 14000 K $\theta_e \sim 1$ and equilibrium is reached, between 6500 K and 14000 K T_e is slightly higher than T_h and below 5500 K, it varies drastically with T_h . It can be noted that T_e is very sensitive to any change in the slope of the curve $n_e(T_e)$. Correlatively T^* is about T_e between 6000 K and 14000 K and T_h below 4000 K. T^* exhibits a strong variation between 4000 and 6000 K.

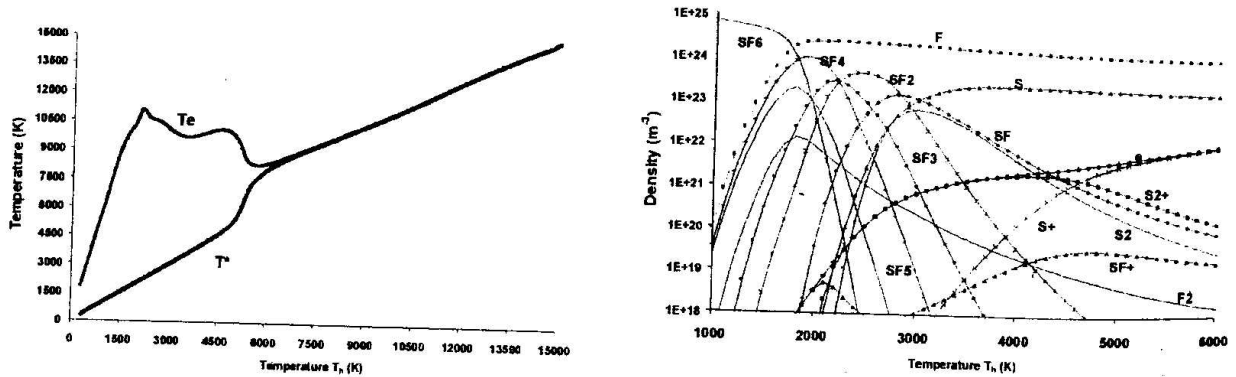


Fig 2: Evolution with heavy species temperature T_h of the electron temperature T_e and intermediate temperature T^* . **Fig3:** Evolution with heavy species temperature of the species densities calculated by using multi-temperature Gibbs free energy minimization at T^* .

When comparing fig 1b and fig 3 representing the multi-temperature composition: S^+ in fig 3 is between one and two orders of magnitude higher than at equilibrium and it exists over 10^{18} m^{-3} down to 3100 K against 3900 K at equilibrium; SF^+ which did not exist at equilibrium, reaches $5 \cdot 10^{19} \text{ m}^{-3}$ at 5000 K; S_2^+ is almost 2 orders of magnitude higher and exists down to 2000 K against 2600 K at equilibrium; F^- has completely disappeared, the charge balance below 4000 K being made by the electrons. Beside that, the neutral species are about the same as at equilibrium. The disappearance of F^- as well of S^- is probably due to the exponent $1/\theta_e$ in the corresponding K_p . When calculating the same composition but with no $1/\theta_e$ in the K_p of ionized species, F^- and S^- exist again with a value slightly higher than at equilibrium.

3.3. Kinetic calculation

The used method is that described in [15]. The kinetic calculations have been performed at T^* .

3.3.1. Complete calculations

Fig 4a represents the species densities evolution with T_h . The complex molecules FSSF and SSFF have not been taken into account due to the lack of data. Over 6000 K, there is not much differences between both equilibrium and multi-temperature calculations. The main differences between kinetic calculations and the two other calculations show up mainly for S^+ , S_2^+ , F^- , S^- and SF^+ species. Compared to equilibrium S^+ shows up over 10^{18} m^{-3} at a temperature of about 100 K lower and its slope increases drastically over 5000 K. The difference with equilibrium reaches more than one order of magnitude at 6000 K. Of course over 4800 K all the electrons come from S ionization. F^- starts, as at equilibrium, at 2600 K but over 3000 K it is slightly higher than at equilibrium and compensated by S_2^+ . Over 3900 K it decreases slightly compared to S_2^+ , which starts to diminish at 4700 K and becomes lower than F^- around 5000 K; S^- is higher than at equilibrium. Over 4000 K SF becomes smaller than at equilibrium with a change in its slope at 5200 K; S_2 is also lower than at equilibrium below 4000 K. SF^+ shows up at 4400 K (there is none at equilibrium) but it is still only $4 \cdot 10^{18} \text{ m}^{-3}$ at 6000 K. S^- and F^+ appear at 5300 and 5500 K, respectively but remain below 10^{19} m^{-3} . The rather good agreement between equilibrium and kinetic calculations is due to the fact that below 4500 K T^* is very close to T_h and over 6500 K T^* is equal to T_e which is not very different from T_h and tends smoothly towards T_h , the equilibrium being reached at 14000 K. When comparing with fig 3 (multi-temperature) the differences are drastic for S^+ , SF^+ , S_2^+ and F^- . For more details see section 3.2.

3.3.2. Calculations neglecting charge loss reactions

The kinetic calculations when neglecting the charge loss reactions are shown in fig 4b. As could be expected when neglecting the following reactions : $S^- + S^+ + F \rightarrow S_2 + F$, $F^- + S^+ + F \rightarrow SF + F$, $SF^+ + e \rightarrow S + F$, $S_2^+ + e \rightarrow 2S$, $S_2^+ + F + F \rightarrow S_2 + 2F$, $S_2^+ + F^- + F \rightarrow SF + F + S$, $S_2^+ + F^- + F \rightarrow S_2 + F_2$, $S_2^+ + F^- + F \rightarrow 2SF$, over 1500 K ionization is due to the formation first of SF^+ and then of S_2^+ which are compensated exclusively by F^- which reaches $8 \cdot 10^{22} \text{ m}^{-3}$ at 2500 K (very high value : 3 % of the neutrals). F^- is probably due to the trapping of electrons by F (all reactions where electrons recombine with ions being eliminated as well as the reactions of F^- with ions). Electrons start to appear at 2000 K and increase drastically up to 2500 K and more slowly over that temperature while F decreases. Contrarily to what has been shown for N_2 or H_2 [15] the composition is far from that obtained with the multi-temperature method.

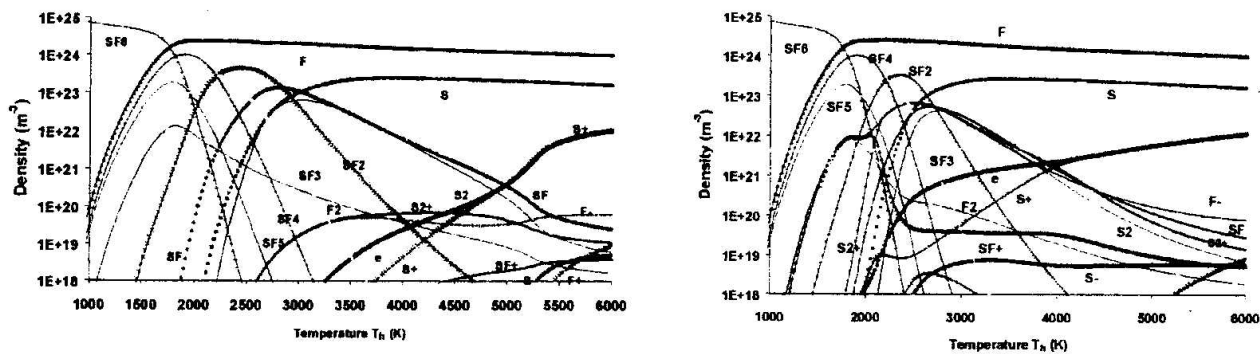


Fig 4.: Evolution with heavy species temperature T_h of the species densities calculated a/ complete calculations, b/neglecting charge loss reactions.

4- Conclusion

The method developed to calculate the kinetic composition of H_2 or N_2 plasmas has been extended to SF_6 plasmas where 33 reactions are involved instead of 7 in the two previous cases. It consists of establishing a relationship between the electron temperature T_e and the heavy species temperature T_h . The ratio T_e/T_h varies as a function of the logarithm of the ratio n_e/n_e^{\max} , n_e^{\max} being the electron density in the plasma core for which equilibrium is established ($n_e^{\max} \sim 10^{23} \text{ m}^{-3}$). The kinetic calculations have been performed by assuming the micro-reversibility between the backward and forward kinetic coefficients using a temperature T^* between T_e and T_h determined as a function of the ratio of electron flux to that of neutral

species. Contrarily to what happens with N_2 and H_2 plasma, where the main differences between equilibrium and kinetic calculations occur between 1500 and 9000 K, with SF_6 the main differences show up between 1500 and 6000 K and are related to the populations of S^+ , S_2^+ , SF^+ , F^- and S^+ species.

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